Solution equilibrium between two structures of Perylene-F_2TCNQ charge transfer co-crystals

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Abstract

We report on the solution growth of the two known structures of perylene/F_2TCNQ charge transfer complexes. The transformation accompanied by a marked morphological change from needle 1:1 to platelet 3:2 crystal structure is observed in the mother liquor. Lattice phonon Raman spectroscopy is used for an easy structure identification of the different morphologies before and after the process. X-ray and lattice phonons spectra of reference samples obtained by physical vapor transport is used to identify the two complexes. A fully spectroscopic analysis of the intramolecular Raman modes is presented to estimate the degree of ionicity, which is found to agree with the value previously reported.

Keywords: A2. Growth from solutions; A1. Raman spectroscopy, B1. charge transfer complex; A1. Lattice phonons

1. Introduction

In the field of organic electronics, research has been initially focused on the semiconducting properties of molecular crystals made by neutral π-conjugated molecules [1]. More recently, several groups have extended the study to another class of systems known as charge transfer (CT) crystals [2], made up of electron donor (D) and acceptor (A) molecules, which, depending on the crystal structure and stoichiometry, can behave as metals or as semiconductors. For instance, a renewed interest has arisen about the well known tetrathiafulvalene-7,7,8,8-tetracyanoquinodimethane (TTF-TCNQ) CT crystal, discovered in 1973 and reported to be the first organic metal. Indeed, it has been demonstrated that charge injection efficiency in organic field effect transistors (OFETs) is improved by the use of an *organic metal-organic semiconductor* interface [3]. This has suggested the employment of organic metals such as TTF-TCNQ [4,5] to improve the performance of an organic semiconductor with respect to devices with silver or gold contacts, even though the intrinsic conductivity of the organic metals is still much lower than that of the inorganics [6].

Notwithstanding the interest for metallic CT systems, also the class of semiconducting crystals in which D and A molecules alternate along one direction (mixed stack CT cocrystals) appears to display appealing properties [7,8]. It has been shown that while single molecule crystals often have unipolar semiconducting behaviour, the mixed stacks CT complexes may exhibit ambipolarity [7], among a wide range of different characteristics [2]. Predictably, the properties of a CT material strongly depend not only on the choice of the pair of molecules acting as charge donor (D) and acceptor (A), but also on their crystal packing arrangements either in the bulk or in the thin film phases.

A number of works have described mixed stack binary systems based on the donor Perylene together with either TCNQ or its fluorinated derivatives as acceptors [9–12]. Electronic and optical properties of such complexes depend on their structure through the stoichiometric ratio between the two components. So much, that in the current literature [11,13] such a situation has led led to define these DA complexes as stoichiomorphs, specifically to indicate different crystal forms determined by different ratios.

In a previous paper, we have shown how to achieve the growth by the physical vapor transport (PVT) method either of the 1:1 or of the 3:2 Perylene/2,5-Difluoro-7,7,8,8-tetracyanoquinodimethane (F_2TCNQ) structure, selectively and with a good yield, just by changing slightly the temperature of the cold end of the apparatus [11]. Here, we report on the growth from solution of the same two structures both obtained by mixing equimolar quantities of Perylene and F_2TCNQ. We have observed and report here that initially needle-like crystals of the 1:1 structure are formed, but that when left in the mother liquor for about 7 days, these needle crystals undergo a change in morphology to platelets. We have investigated the nature of this transformation by Raman and X-ray, showing that it implies the formation of the 3:2 structure. The 1:1 cocrystal is then the one kinetically favored in the starting conditions (temperature and stoichiometric ratio). The subsequent transformation must imply a slower process occurring at the crystal-solution interface.

The structural identification is carried out by analyzing the lattice vibrations (phonons), which probe the crystal packing identity [14] over the low wavenumber range (10-150 cm^{-1}). Lattice modes have been already successfully employed in the recognition of

polymorphs in the field of organic semiconductors [14–16] and of pharmaceutics [17]. However, in this specific case, the occurrence of different structural arrangements is linked to different stoichiometries. Therefore, the low energy vibrational spectra, where lattice phonons are observed, together with internal modes strongly coupled with them, are highly distinctive of the various crystal forms, as recently reported also for the Perylene-TCNQ complexes [9]. While lattice phonons uniquely identify different crystal structures, the higher wavenumber (> 150 cm^{-1}) internal modes originate instead all from the same molecular species. Thus, regardless of which stoichiometries occurs, they undergo only frequency shifts, that depend on the specific geometry of each DA pair and consequently on the different degree of CT (ρ) in it. Moreover, we use Raman spectroscopy in higher wavenumber range to estimate ρ of the two structures, taking into account the electron-phonon coupling (*e-mv*), confirming the values previously obtained [11] through infrared (IR) spectroscopy.

2. Materials and methods

2.1 Crystal growth.

Perylene (Sigma Aldrich, purity 99%) and F_2TCNQ (Tokyo Chemical Industry, purity 98%) were purified by sublimation in a final nitrogen vacuum to prevent chemical degradation. Toluene and Acetonitrile (Sigma Aldrich) of spectroscopic grade were employed for the solutions. The formation of the CT crystals has followed a procedure inspired to the one adopted in Ref. [13] for the formation of Perylene-TCNQ. Equimolar amounts of perylene and F_2TCNQ were dissolved in a solvent mixture of toluene/acetonitrile (5/1), sonicated for 15 minutes and then kept in a temperature-controlled aluminum heating block at 333 K for one hour to ensure the complete

dissolution of the parent compounds. This yielded a transparent yellow solution which was left to cool down to RT in a sealed vial. Overnight black needle-like single crystals were obtained. Some were removed from the mother liquor, washed with fresh cooled solvent and dried. Those left behind in the liquor disappeared over a time span of ca 7 days at ambient conditions, and the growth of platelet-like crystals was observed.

2.2 Raman spectroscopy.

The Raman spectra over the energy range 10-2500 cm^{-1} were recorded with a JY-Horiba T64000 triple Raman spectrometer interfaced to an Olympus BX40 microscope with 50× or 100× objectives, working in backscattering configuration. This setup allowed for a lateral resolution of ≈ 1 μm, with a theoretical field depth ranging from about 7 to 25 μm. Excitation was provided by a Kripton ion laser tuned at 647.1 nm, a wavelength long enough to prevent fluorescence emission of the studied systems. The polarization of the incident laser radiation was controlled by a half-wave polarization rotator, and the scattered light was analyzed by a rotating wire-grid polarizer. When needed, the impinging power was reduced with suitable optical density neutral filters to avoid sample damage.

2.3 X-Ray diffraction measurements.

Single crystal diffraction data for the Perylene: F_2TCNQ 3:2 structure were collected at 150 K on a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation λ = 0.7107 Å. Unit cell determination, data scaling, and corrections for Lorentz and polarization effects were performed with Denzo-SMN [18]. A symmetry-related (multi-scan) absorption correction was applied. Crystal parameters are provided in Table 1. Structure solution, followed by full-matrix least-squares refinement, was performed using the WINGX-v2014.1 [19] suite of programs throughout. Hydrogen atoms were

placed onto calculated positions and refined using a riding model. Fluorines F1 and F4 are refined with 50% occupation. The crystal was poorly diffracting at high angles which lead to a high R(int) and R-value and data above 2 Θ=48° had to be truncated. Therefore, the structure is just a means of comparing data with the Raman measurements. Crystallographic CIF file for the reported structure is given in the supplementary information.

Table 1 Crystal data and structure refinement for 1:1 (Ref [11]*) and 3:2 (this work) Perylene-F_2TCNQ complexes.*

Perylene:F_2TCNQ	**1:1**	**3:2**
Empirical formula	$C_{32}H_{12}F_2N_4$	$C_{84}H_{40}F_4N_8$
Formula weight	490.46	1237.24
Temperature	150(2) K	150(2) K
Wavelength	0.7107 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	P-1
Unit cell dimensions	a = 7.0425(10) Å α= 90° b = 8.4114(9) Å β= 96.086(6)° c = 19.117(3) Å γ= 90°	a = 7.2268(5) Å α= 112.264(4)° b = 19.1439(14) Å β= 90.280(4)° c = 22.2779(12) Å γ=93.904(3)°
Volume	1126.1(3) Å^3	2844.2(3) Å^3
Z	2	2
Density (calculated)	1.447 Mg/m^3	1.445 Mg/m^3

3. Results and discussion

The binary system Perylene-F_2TCNQ has been reported to crystallize in two different structures with 1:1 and 3:2 stoichiometry between donor and acceptor molecules [11]: the corresponding packing arrangements for the two species are shown in Figure 1. The 1:1 structure is monoclinic with symmetry $P2_1/n$ and exhibits two alternating stacks along the *a* axis, with different orientations in the plane *bc*. The regular stacks show a D-A distance of 3.28 Å with a slight deviation between the molecular planes of Perylene and F_2TCNQ of 2.37° for both oriented stacks.

The 3:2 structure crystallizes in a triclinic system with symmetry P-1. The structure is made up by DAD trimers arranged in a quasi-one-dimensional stack parallel to the *c* axis,

while DA dimers are located along the *a* axis approximately perpendicular to the trimer layer, at the same intra-stack distance characterizing the 1:1 co-crystal. Analyzing in details the stacks, one can actually identify two different types of trimers with tilt angles between perylenes and F_2TCNQ planes of 1.75° and 1.89°, respectively. In the dimers the planes are almost perfectly parallel, with an angle of 0.52°.

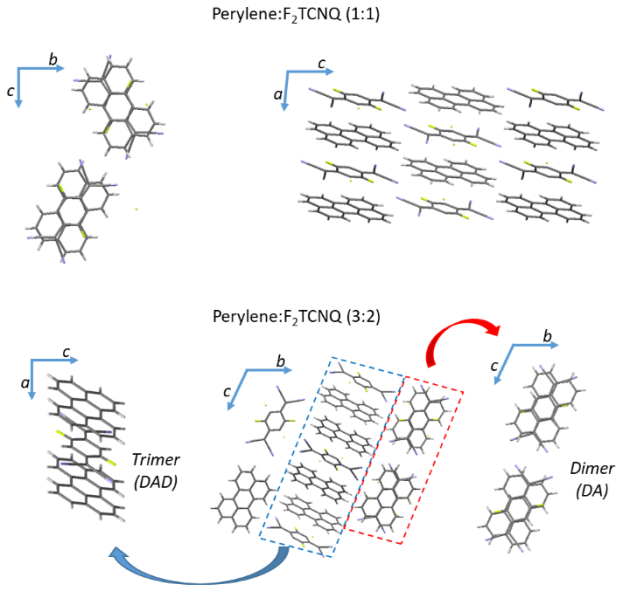

Figure 1 X-ray structures comparison of Perylene-F_2TCNQ 1:1 (top) and 3:2 (bottom) structures.

Generally, charge transfer complexes are highly insoluble and to obtain crystals with suitable dimensions for single crystal x-ray diffraction measurements the growth method of choice is PVT or other vapor-based techniques. For the perylene-F_xTCNQ family several groups have reported the growth of various structures with different fluorinated TCNQs by PVT, both in closed [11] and in open systems [12,20]. Furthermore, also solvated crystals have been obtained in the case of Perylene/F_4TCNQ [11], whereas different polymorphs of the 1:1 Perylene-TCNQ system have been obtained by changing the conditions in the PVT method [21]. Up to now, solution methods have been applied only to the perylene-TCNQ binary systems [10,22–24]. Hu and coworkers have reported

how the perylene-TCNQ 1:1 and 3:1 structure growth is solvent-dependent [10], while Zhu et al. have shown the influence of the donor concentration on the equilibrium between high and low ratio structures [24].

Single crystals of the Perylene-F_2TCNQ system in this work were obtained from the same solution as described in section 2, with two different morphologies: needles in the fresh precipitate, and platelets by letting the precipitate to remain, in the mother liquor (figure 2).

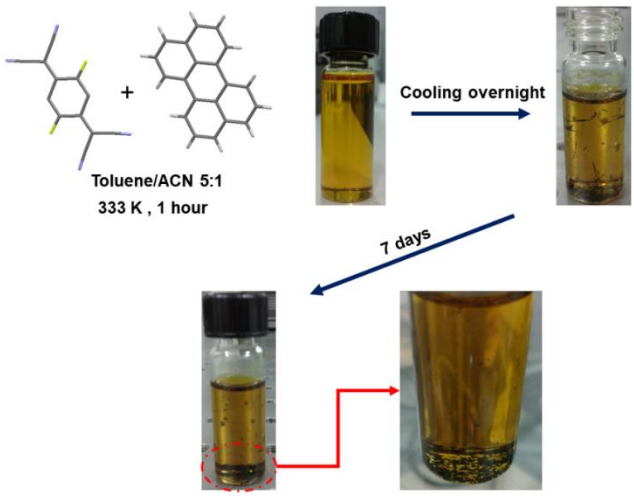

Figure 2 transformation of the crystals observed with time in solution.

The two obtained crystalline forms have been identified by micro-Raman spectroscopy. In Figure 3a we report the low frequency Raman spectra of the needle and platelets samples whose images are shown in Figures 3b and 3c.

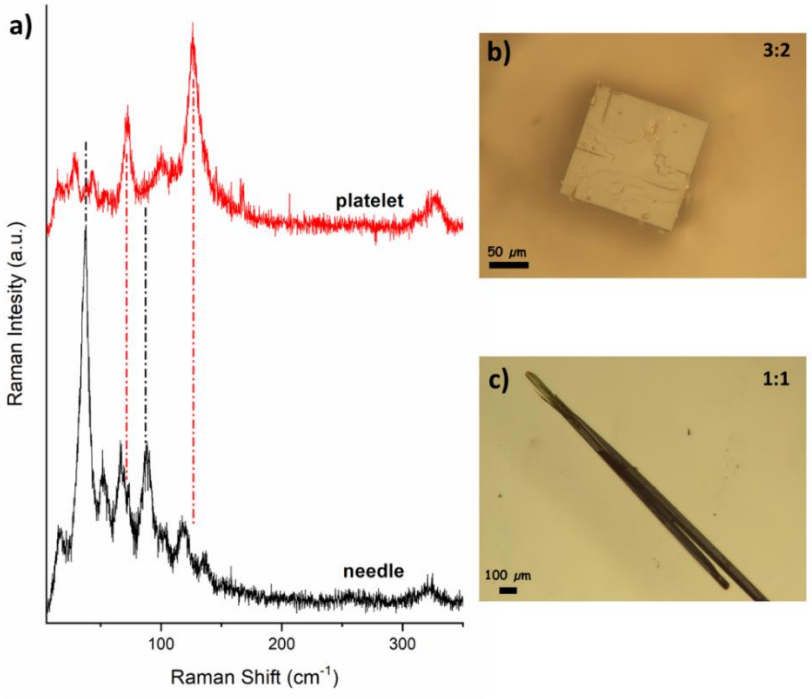

Figure 3 Lattice phonons Raman and crystal morphologies of the Perylene-F_2TCNQ complexes. Vertical lines highlight the main peaks of 1:1 (black) and 3:2 (red) structures.

The different spectral patterns displayed by the two morphologies immediately suggest that we are dealing with different polymorphs or structures. Indeed, while the intramolecular modes are sensitive to the chemical identity, which remain the same in the different crystal structures, lattice phonon modes embody intermolecular interactions and correspond to collective translational and/or rotational motions of the molecules in the unit cell. Lattice phonons, in other words, represent the fingerprint of the specific crystal lattice. Each structure has a distinctive lattice dynamic which corresponds to its own unique spectral pattern. A complete analysis of the polarized lattice phonon spectra reported in Figure S1 allow us to exclude any accidental degeneration in the analyzed crystal specimens. The platelets were structurally characterized by single crystal x-ray diffraction and were found to belong to the 3:2 structure (Table 1). Because of the poor crystal sample quality, the same analysis was not possible for the needles. However, to confirm the 1:1 structure their lattice phonon spectra were compared to those of the samples obtained by PVT and characterized in a

previous work [11] further stressing the importance of lattice phonons as a diagnostic tool for structure recognition.

The Raman spectra of the internal modes, shown in Figure 4, can be assigned with reference to the spectra of the two parent compounds Perylene and F_2TCNQ, but a number of features confirms the findings from the low frequency spectra. For instance, as already reported for the infrared spectra [11], the 1:1 structure presents only one peak at 1449.6 cm^{-1}, arising from the unique DA pair of the packing and assigned to a C=C stretching mode of the F_2TCNQ molecule. The 3:2 structure instead displays a doublet for the same vibration with peaks at 1450.2 and 1445.6 cm^{-1}, assigned to the dimer (DA), as reasonably inferred from the result in the equimolar ratio structure, and to the trimer (DAD), respectively. Different frequencies originate from different mutual molecular orientations in the complexes and from their slightly different ionicity. Besides, in the trimer stacks for any two molecules of donor there is one molecule of acceptor, which implies a distinct pattern of intermolecular interactions compared to the equimolecular case.

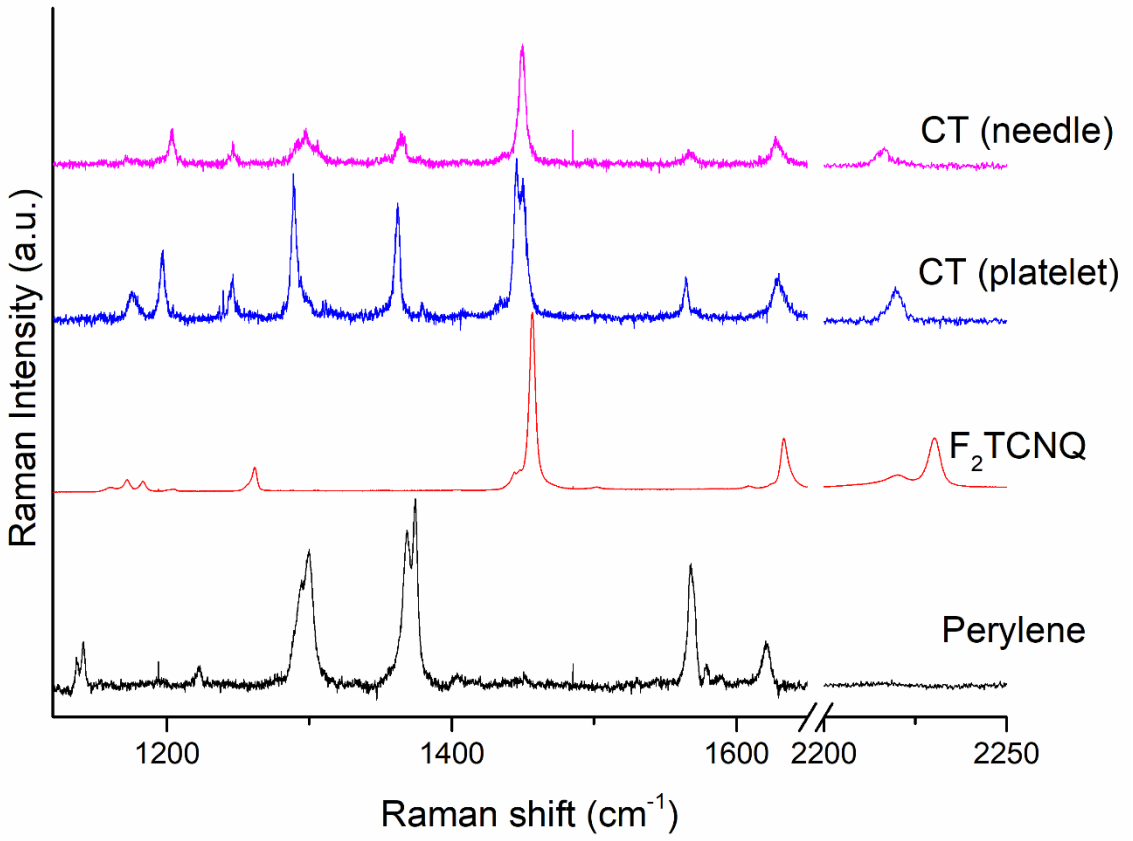

Figure 4 Raman spectra in the energy range of the internal vibrations for the Perylene and F_2TCNQ parent compounds and for the 1:1 and 3:2 CT complexes.

It is well known how by using IR spectroscopy it is possible to estimate the degree of charge transfer ρ in mixed stack (*ms*) DA systems [11,25–27], while Raman spectra are dominated by the totally-symmetric (in the molecular symmetry) modes, whose frequency is affected by the interaction with the CT electrons (e-mv interaction) [28]. As a consequence, whereas in IR one can expect (and find) a linear relationship between ρ and the frequency shift of the charge sensitive vibrations like the TCNQ C=C stretchings, in Raman spectroscopy the dependence is not linear. The *e-mv* coupling [28,29] produces a frequency lowering larger than what would be expected from the degree of ionicity ρ computed via the non-totally symmetric vibrations. Thus, in using Raman spectroscopy to evaluate ρ for the two structures of the donor-acceptor complex perylene-F_2TCNQ, the effect of *e-mv* coupling must be taken into account.

Considering a regular *ms* arrangements in the "isolated band" approximation [30] and assuming no interaction between the C=C vibration and the other total symmetric modes, the dependence of the frequency of a specific mode with ρ, for ρ < 0,5, is given by:

$$\Omega_n = \omega_n - 2g_n^2\rho\frac{(1-\rho)^2}{\omega_{\mathrm{CT}}} \qquad \text{eq. 1}$$

Here ω_n and Ω_n are the frequencies of the unperturbed and e-mv perturbed n-th mode, respectively, g_n is the *e-mv* coupling constant and ω_{CT} is the frequency of the charge transfer electronic transition. ω_n can be related to the ω_0 frequency value of the neutral molecule through the ionization frequency shift $\omega_n = \omega_0 - \Delta\rho$, thus obtaining:

$$\Omega_n = \omega_0 - \Delta\rho - 2g_n^2\rho\frac{(1-\rho)^2}{\omega_{\mathrm{CT}}} \qquad \text{eq. 2}$$

For the previously mentioned C=C stretching mode, ω_0 = 1457 cm^{-1} and the ionization frequency shift $\Delta\rho$ = 37 cm^{-1} as obtained from neutral and full ionic F_2TCNQ spectra reported in Figure S3. The relevant *e–mv* coupling constant g can be estimated experimentally or calculated following the procedure in ref [30,31]. In this case we conveniently use the same value of the unfluorinated TCNQ molecule, ≈ 65 meV (524 cm^{-1}) [28], assuming the *g* does not vary significantly in going to F_2TCNQ. A reasonable value for the CT transition ω_{CT} can be assumed to be ≈ 6800/7000 cm^{-1} (0.85 eV) [11]. This yields the ρ/Ω relationship reported as a continuous curve in Figure 5. Note that the dashed line given in the same figure indicates the linear dependence of the frequency on ρ in the absence of *e–mv* coupling and allows for an estimate of the error affecting the charge transfer value when the coupling is neglected.

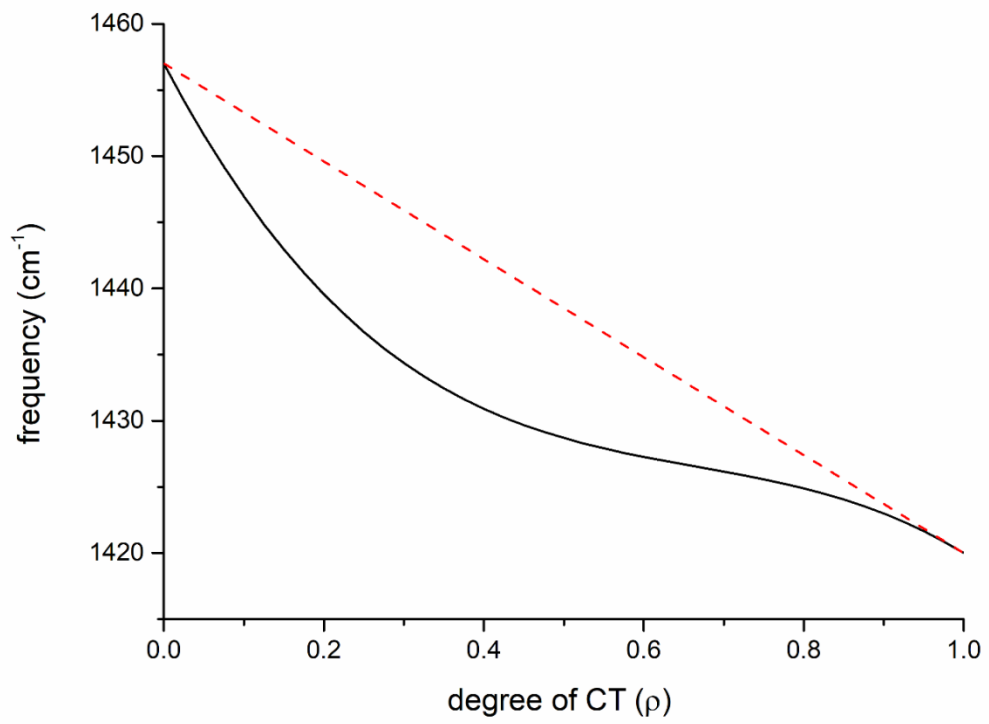

Figure 5 Frequency Ω_n of the F_2TCNQ C=C stretching mode given as a function of the charge transfer ρ, computed by considering the e–mv coupling (black line) and in the absence of the interaction (dashed red line).

Following the equation 2 given above, the Raman frequency of 1449,6 cm^{-1} of the 1:1 structure corresponds to a ρ value of 0.1, while the doublet of the 3:2 at 1450.2 and 1445.6 cm^{-1} corresponds to ρ = 0.1 and 0.15, respectively, in agreement with the reported values estimated by infrared spectroscopy in the previous work [11]. Furthermore, the Raman measurements confirm that the interactions between donor and acceptor are stronger in the 3:2 complex, because of the formation of the trimeric stacks. Altogether, these results demonstrate that Raman spectroscopy can be satisfactorily used to estimate ρ provided that the effect of *e-mv* interaction is properly taken into account.

4.Conclusions

The 1:1 and 3:2 structures of the Perylene-F_2TCNQ CT complex have been found to be related by equilibrium in solution. When starting from equimolecular quantities of the

parents compounds, the 1:1 complex is the first to form but the permanence in the solution transforms it into the 3:2 complex, demonstrating that the latter is the one derived from slower crystallization in the operating conditions, whereas the 1:1 stochiomorph is the one favoured at higher temperature or by a kinetic process. The transformation is detected via a marked morphology change, needles and platelets respectively, and it has been confirmed by lattice phonon Raman spectroscopy, which allowed for a fast structure recognition. The two structures had been previously selectively synthesized by the PVT method, obtaining the 1:1 system at a deposition temperature lower than the 3:2 system. We note that different structures in perylene/TCNQ have been obtained from solution either by using different solvents and crystallization procedure, or by using different concentrations of the two components.Thus the Perylene-F_xTCNQ series is proven to be the flawless playground for the study of polymorphism and different organization of donor-acceptor molecules in CT crystals.

Acknowledgments

The authors thank Dr. Enrico Da Como for helpful discussions.

Supporting Information

Polarized Lattice phonons and intramolecular spectra, Raman intramolecular modes of F_2TCNQ^0 and $K^+F_2TCNQ^-$.

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